

# PATENT ABSTRACTS OF JAPAN

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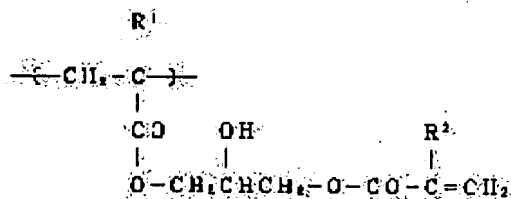
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## (54) WATER-SOLUBLE PHOTSENSITIVE COMPOSITION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To enable development with water, to use no bichromate, to enhance photosensitive, corrosion resistance, resolution, and strippability by incorporating a block copolymer obtained by adding specified structural units to a poly vinyl alcohol component and a photosensitive agent.

**SOLUTION:** This photosensitive composition contains a phgoto-sensitive agent and a block copolymer comprising polyvinyl alcohol component and structural units represented by the formula in which each of R1 and R2 is, independently, H atom or methyl group The block copolymer to be used is formed by adding (meth) acrylic structural units to the terminal of the polyvinyl alcohol main chain. The block copolymer is formed also by radically polymerizing (meth)acrylic and in the presence of a polyvinyl alcohol having mercap to groups and adding glycidyl (meth)acrylate.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the water-soluble photosensitivity constituent used for photoresists, such as an electronics product. In more detail, using water, development is possible for this invention, and it relates to the water-soluble photosensitivity constituent which does not contain dichromate.

[0002]

[Description of the Prior Art] In recent years, as for integrated circuits, such as a semiconductor IC and LSI, a degree of integration becomes still higher, and more detailed processing is needed. In connection with this, more detailed processing is demanded also of the metal component. There are semi-conductor components, such as display device components, such as components for the electron tubes, such as a shadow mask for color TV and a color filter for the camera tubes, and a filter for electrochromatic displays, a color filter for CCD, a leadframe, and a photo mask, other computer associated parts, household electric appliances, camera components, etc. in these common-names photofabrication, and the application is large.

[0003] There are the machining method and a chemical-machining method in these processings. A chemical-machining method applies a photosensitive resist to a need metal, and can be burned on this in an image through a photo mask with a xenon LGT and a high pressure mercury vapor lamp. subsequently, the unexposed part of a resist is eluted, the metaled skin is exposed, it is etched and processed with an etching reagent, and precision is alike and higher than machining.

[0004] As a photosensitive resist used for such processing, there are an organic solvent meltable mold and a water meltable mold. Although there are a cyclized-rubber system, a novolak system, a cinnamic acid system, etc., the former is not desirable to labor environment and earth environment in order to use an organic solvent. Although there are PVA, casein, and a fish GURYU system in the water-soluble type of the another side latter, in order to use dichromate as a sensitization agent, great cost and a great effort are needed for waste fluid processing of hexavalent chromium. Moreover, in order to use dichromate, colloid receives oxidation, and the definition and shelf life of sensitization liquid are bad. Without using dichromate also from this point, resolution is high by the water-soluble type, and, moreover, the resist which was excellent in corrosion resistance with high sensitivity is called for.

[0005]

[Objects and Summary of the Invention] The purpose of this invention is to offer the resist which development is possible for and was excellent in photosensitivity excluding dichromate, and whose resolution was high and was excellent in corrosion resistance, or the water-soluble photosensitivity constituent which can exfoliate easily at the time of exfoliation using water.

[0006] In order to solve said technical problem, as a result of inquiring wholeheartedly, by introducing a metaglycidyl acrylate (meta) addition product structural unit into a vinyl alcohol system polymer component, this invention persons acquire knowledge that these technical problems can be solved, and came to complete this invention.

entrainment opening of a reaction container, it cooled to the room temperature, with nitrogen introduced, and pH was adjusted to 3 by 1 N-H<sub>2</sub>SO<sub>4</sub>. Subsequently, after having added the acrylic-acid monomer 47 section, equalizing and performing a nitrogen purge further, the temperature up was carried out to 70 degrees C, the initiator was added, and the polymerization was performed. Addition of an initiator performed under churning the water solution which dissolved the potassium-bromate 2.3 section over [ dropping funnel ] 3 hours at 70 degrees C in the distilled water 35 section. Subsequently, reaction mixture was cooled to the room temperature and the PVA-Pori (acrylic acid) block-copolymer water solution was obtained. The infrared absorption spectrum of the obtained block copolymer is shown in drawing 1. After measurement fully washed the polymer and carried out reduced pressure drying by isopropyl alcohol, it was performed by considering as a water solution again and making it the shape of a film.

[0045] (Addition of glycidyl methacrylate) The obtained block copolymer was adjusted to pH4.0, the triphenyl benzonium chloride 1.5 section was added as the glycidyl methacrylate 92 section and a reaction catalyst, the 4-t-butyl pyrocatechol 5.7 section was added as polymerization inhibitor, the reaction was performed at 80 degrees C for 6 hours, and the block-copolymer water solution which added glycidyl methacrylate was obtained. This block-copolymer water solution was the transparency liquid of light yellow, and viscosity [ in / in pH / 5.2 or 25 degrees C ] was 300 mPa·s. The infrared absorption spectrum of this block copolymer obtained like the above is shown in drawing 2.

[0046] (Production of the sensitization resist film) Next, the distilled water 16.4 section, 4, and 4-bis (dimethylamino) benzophenone 0.02 section, the benzyl 0.03 section, and the ethyl alcohol 16.7 section were added to the block-copolymer (15% water solution) 67 obtained section, and sensitization liquid was prepared. This sensitization liquid was degreased, the spin coater was used and applied to 42 alloy plate (iron-nickel alloy) which performed rustproofing, it dried for 10 minutes at 70 degrees C, and the sensitive plate was obtained. The thickness of a sensitization layer was 7 micrometers.

[0047] (Exposure-development) 2 was exposed for the obtained sensitive plate cm 30mm J /with the metal halide lamp on vacuum pressure arrival using the resolution test mask and the mask for sensitometries (the Fuji step guide P, 2.15 to 0.15 15 steps of concentration regions). Subsequently, spray water development for 15 seconds was performed using tap water, and various evaluations were presented. A result is shown in Table 1.

[0048] The PVA system block copolymer which added glycidyl methacrylate was manufactured like the example 1 except the component presentation and reaction condition which are shown in the after-mentioned table 1 having performed addition of the glycidyl methacrylate to manufacture and this of a [examples 2-5] PVA system block copolymer. The description of the water solution of the obtained copolymer is combined and shown in Table 1. Furthermore, after preparing sensitization liquid like an example 1 using this block copolymer, the sensitive plate was obtained, and negatives were developed further, and various evaluations were presented. A result is shown in Table 1.

[0049] The resist was not able to be obtained, although the block copolymer used in the [example 1 of comparison] example 1 was changed into PVA-105 (Kuraray Make, degree-of-polymerization 500, and saponification degree % of 98.5 mols) and preparation of the sensitization resist film was tried similarly.

[0050] the [example 2 of comparison] PVA-205 (Kuraray Make, polymerization-degree 500, and saponification degree % of 88.0 mols) 15 section -- the distilled water 85 section -- warming -- it dissolved and the PVA solution was prepared. Subsequently, after cooling, it filtered, after adding the dichromic acid Amon 0.75 section in the preparation PVA solution and dissolving, and it considered as sensitization liquid. 42 alloy plate (iron-nickel alloy) was pretreated like the example 1, and after applying sensitization liquid and drying, 2 was exposed cm 30mm J /. Although negatives were developed with tap water for 15 seconds after an appropriate time, an image is not made, but it is whole surface \*\*\*\*\*.

[0051] Except having exposed the example 2 of the [example 3 of comparison] comparison by 2 cm 240mm J /, the sensitization resist film was obtained similarly. Moreover, the same evaluation as an example was performed. A result is shown in Table 1.

[0052]

[Table 1]

	実 施 例					比較例
	1	2	3	4	5	3
(ブロック共重合)						
末端メルカプト基含有PVA(部)	100	100	100	100	100	
蒸留水(部)	935	935	935	935	935	
アクリル酸(部)	47	40	59	40	40	
アクリルアミド(部)	—	30	—	—	—	
ダイアセトンアクリルアミド(部)	—	—	21	—	—	
過硫酸アンモニウム(部)	—	—	—	0.4	—	
臭素酸カリウム(部)	2.3	2.3	2.3	2.3	2.3	
(付加反応)						
メタクリル酸グリシジル(部)	92	80	117	96	96	
トリエチルベンジルアンモニウムクロライド(部)	1.5	1.3	1.9	1.4	1.4	
ブチルカテコール(部)	5.7	5.7	5.7	3.0	3.0	
反応温度(℃)	80	80	80	80	80	
反応時間(h)	6	6	6	6	6	
(反応液)						
反応液の外観	淡黄色透明液	淡黄濁液	淡黄濁液	黄色透明液	淡黄色透明液	
反応液のpH	5.2	4.7	5.3	5.0	5.1	
反応液の粘度(mPa・s)	300	247	190	58	56	
(結果)						
レジスト膜のタック性	無し	無し	無し	無し	無し	無し
現像性	○	○	○	○	○	○
感度(ステップガイドによる)	4段	4段	4段	4段	4段	3段
解像度(μ)	4	6	4	6	6	25
硬膜時の接着性	○	○	○	○	○	○
レジストの耐食性	○	○	○	○	○	○
膜厚(μ)	7	7	7	7	7	7

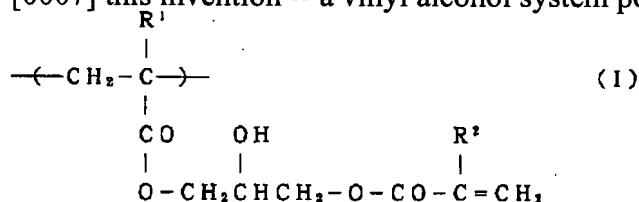
Viscosity of notes reaction mixture: 25 degrees C of evaluations of a Brookfield viscometer and the photopolymer film obtained in addition in each example and the example of a comparison were performed as follows.

[0053] The water shower (1kg/cm<sup>2</sup>) was used for the sensitive plate after development nature exposure, non-\*\*\*\* was probed, time amount until a metal substrate appears was measured, and the following criteria estimated development nature.

[0054] O; the step guiding method for finding with how many steps of the light the light of a constant rate was hardened by irradiating the photopolymer film through the mask which exceeded less than 30 seconds and \*\*,30 second, and gave the gradual translucent concentration difference in super-sensibility development for less than 120 seconds, and x; 120 seconds estimated sensibility. This translucent mask is concentration 0.15-2.15, and has a concentration difference one by one to 15 steps every concentration 0.15, and when it is one step, as for 1.4 times and two steps of cases, one 2.0 times the sensibility of this is shown [ step / zero ] from zero step. Sensibility is so high that this number of stages is high, and two or more steps can usually present practical use as a resist.

[0055] Bat immersion for 1 minute in a hardening solution (molybdic-acid Amon 5%, 5% of phosphoric acids, 90% of purified water, 10-30 degrees C of solution temperature) was performed for the image

[0007] this invention -- a vinyl alcohol system polymer component and a bottom type (I) -- [Formula 2]



A block copolymer including the structural unit expressed with (R<sup>1</sup> and R<sup>2</sup> show hydrogen or a methyl group separately respectively among a formula) and a list are provided with the water-soluble photopolymer constituent which comes to blend a sensitization agent at this. Moreover, this invention offers the water-soluble above-mentioned photosensitivity constituent which carried out the gestalt of a water solution, or the gestalt of a film.

[0008] The acrylic-acid system structural unit as which the block copolymer used in this invention is expressed in the principal chain end of a vinyl alcohol system polymer component by said formula (I) (meta) is added. The structural unit expressed with a bottom type (II) besides a formula (I) as a structural unit added here may be included.

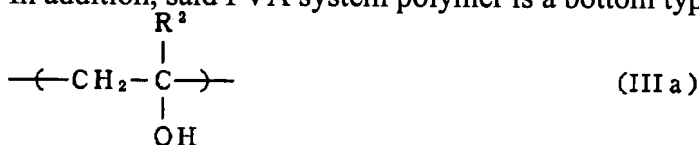
[0009]

[Formula 3]

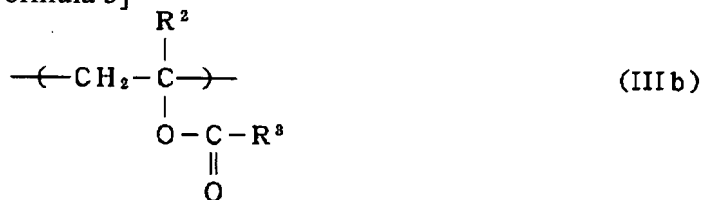


(The inside of a formula and R<sup>1</sup> are the same as the above)

In addition, said PVA system polymer is a bottom type (IIIa) and [Formula 4] (IIIb).



[Formula 5]



It has -S- at the end of a principal chain including the structural unit expressed with (R<sup>2</sup> means hydrogen or the alkyl group of carbon numbers 1-6 among a formula, and R<sup>3</sup> means hydrogen or the alkyl group of carbon numbers 1-20).

[0010] Therefore, this invention carries out the radical polymerization of the acrylic acid (meta) to the bottom of existence of the vinyl alcohol system polymer which has a sulfhydryl group, and offers the water-soluble photosensitivity constituent which blended the block copolymerization and the sensitization agent which come to add metaglycidyl acrylate subsequently (meta).

[0011]

[Detailed Description of the Invention] This invention is explained in more detail below.

[0012] The block copolymer which is the 1st component of the water-soluble photosensitivity constituent of this invention contains the metaglycidyl acrylate addition product structural unit expressed with a vinyl alcohol system polymer (henceforth PVA system polymer) component, and said formula (I) at least (meta). Although this block copolymer can be manufactured by various approaches,

the method of carrying out the radical polymerization of an acrylic acid and/or the methacrylic acid (it being hereafter written as an acrylic acid (meta)), reacting and subsequently (meta), manufacturing metaglycidyl acrylate is the most desirable under existence of the PVA system polymer (henceforth PVA-SH) which has the end sulfhydryl group obtained by saponifying the vinyl ester system polymer which has a thiolic acid ester group at the end typically. Thus, PVA-SH is indicated by JP,6-74304,B and can come to hand by the trade name of M-polymer (Kuraray Make).

[0013] (PVA system polymer-VA-SH which has an end sulfhydryl group) PVA-SH used by this invention saponifies the vinyl ester system polymer which carried out the polymerization of the vinyl system monomer which makes a vinyl ester monomer a subject, and obtained it under existence of thiolic acid with a conventional method, and is obtained.

[0014] The organic thiolic acid which has -COSH radical as this thiolic acid is used. For example, although a thiol acetic acid, a thiol propionic acid, thiol butanoic acid, a thiol valeric acid, etc. are mentioned, especially, resolvability is also good and a thiol acetic acid is the most desirable.

[0015] Moreover, what is necessary is for a radical polymerization to be just possible for a vinyl ester monomer. For example, although formic-acid vinyl, vinyl acetate, propionic-acid vinyl, Valerin acid vinyl, capric-acid vinyl, URARIN acid vinyl, stearic acid vinyl, benzoic-acid vinyl, vinyl pivalate, BASA tick acid vinyl, etc. are mentioned, vinyl acetate is desirable especially from the purpose which obtains a PVA system polymer.

[0016] PVA-SH is the range which does not spoil the meaning of this invention, and the above-mentioned vinyl ester and a copolymerizable monomer are made to live together, and it can also be copolymerized. As such a monomer, for example Ethylene, a propylene, 1-butene, Olefins, such as isobutene, an acrylic acid, a methyl acrylate, an ethyl acrylate, Acrylic-acid n-propyl, acrylic-acid i-propyl, acrylic-acid n-butyl, Acrylic-acid i-butyl, acrylic-acid t-butyl, 2-ethylhexyl acrylate, Acrylic ester, such as acrylic-acid dodecyl and acrylic-acid octadecyl A methacrylic acid, a methyl methacrylate, ethyl methacrylate, methacrylic-acid n-propyl, Methacrylic-acid i-propyl, n-butyl methacrylate, methacrylic-acid i-butyl, T-butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic-acid dodecyl, Methacrylic ester, such as methacrylic-acid octadecyl, the methyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether, n-butyl vinyl ether, i-butyl vinyl ether, t-butyl vinyl ether, dodecyl vinyl ether, Vinyl ether, such as stearyl vinyl ether, acrylonitrile, Nitril, such as a methacrylonitrile, a vinyl chloride, a vinylidene chloride, Halogenation vinyl, such as vinyl fluoride and vinylidene fluoride, an acetic-acid allyl compound, Allyl compounds, such as an allyl chloride, boletic acid, a maleic acid, an itaconic acid, A carboxyl group content compound and its ester, such as a maleic anhydride, phthalic anhydride, trimellitic anhydride, or itaconic acid anhydride, Sulfonic group content compounds, such as an ethylene sulfonic acid, an allyl compound sulfonic acid, a meta-allyl compound sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, Vinylsilyl compounds, such as vinyltrimetoxysilane, isopropenyl acetate, TORIMECHIRU -(3-acrylamide-3-dimethyl propyl)- Ammoniumchloride, 3-acrylamidepropyl trimethylammoniumchloride, 3-methacrylamide propyl trimethylammonium chloride, The quarternary ammonium salt of N-(3-allyloxy-2-hydroxypropyl) dimethylamine, To the quarternary-ammonium-salt pan of N-(4-allyloxy-3-hydroxy butyl) diethylamine, acrylamide, N-methylacrylamide, N-ethyl acrylamide, N,N-dimethylacrylamide, Quarternary ammonium salt, such as diacetone acrylamide, N-methylol acrylamide, methacrylamide, N-methyl methacrylamide, N-ethyl methacrylamide, and N-methylolmethacrylamide, etc. is mentioned. As for the amount of the above-mentioned monomer used, less than [ 5 mol % ] is desirable to said vinyl ester monomer.

[0017] In order to perform the polymerization of the vinyl system monomer which makes vinyl ester, such as vinyl acetate, a subject to the bottom of existence of thiolic acid, a radical polymerization initiator may be used and a bulk-polymerization method, a solution polymerization method, a suspension-polymerization method, an emulsion-polymerization method, etc. may adopt which approach. The solution polymerization method which uses a methanol as a solvent among these is industrially the most advantageous.

[0018] There is especially no limit about the addition to the polymerization system of the thiolic acid made to exist during a polymerization, and the addition approach, and you may choose suitably with the

physical-properties value of the vinyl ester system polymer made into the purpose. As a polymerization method, well-known approaches, such as a batch type, half-continuous system, and continuous system, are employable.

[0019] As a radical polymerization initiator, each well-known radical polymerization initiator, such as - azobisisobutyronitril, and 2 and 2 '2, 2'-azobis (4-methoxy-2,4-dimethylvaleronitrile), a benzoyl peroxide, and peroxidation carbonate, can use it, for example. Moreover, a radiation, an electron ray, etc. may be used.

[0020] Although polymerization temperature is determined by the physical properties of the denaturation PVA made into the purpose, it is usually chosen out of the range of 10-90 degrees C. The initiator then used is suitably chosen according to polymerization temperature. After carrying out a predetermined time polymerization, the vinyl ester system polymer which has a thiolic acid ester group at the end is obtained by removing the vinyl ester of a non-polymerization by the well-known approach.

[0021] Thus, the obtained vinyl ester system polymer can be saponified with a conventional method, and alcohol and especially saponifying in a methanol are usually desirable. Not only an anhydride but the thing of a little water system is used according to the purpose, and alcohol may use together organic solvents, such as methyl acetate and ethyl acetate, if needed. Saponification temperature is usually chosen from the range of 10-90 degrees C. Although alkaline catalysts, such as a sodium hydroxide, a potassium hydroxide, sodium methylate, and a potassium methylate, are desirable and the amount of this catalyst used is suitably decided with size, a moisture content, etc. of a saponification degree as a saponification catalyst, for example, it uses 0.002 or more preferably 0.001 or more by the mole ratio to a vinyl ester unit. It is desirable preferably to carry out to 0.2 or less by the mole ratio -- if the amount of alkali increases too much, it will become difficult to remove residual alkali out of a polymer, and a polymer colors. In addition, it reacts with alkali catalysts, such as a carboxyl group and its ester group, into a vinyl ester system polymer, and when the component which consumes alkali contains, the alkali catalyst of the amount which added a part for the consumption is used.

[0022] According to the above-mentioned saponification reaction, both vinyl ester association of the end thiolic acid ester of a vinyl ester system polymer and a principal chain is saponified, a polymer end becomes a sulfhydryl group and a principal chain becomes vinyl alcohol. The saponification degree of the vinyl ester unit of a principal chain may be suitably chosen according to the purpose of use. The polymer which deposited after the saponification reaction can be refined by the well-known approach of a methanol etc. washing, and can usually be obtained as white powder by removing impurities, such as an alkali-metal salt of residual alkali and an acetic acid, and drying.

[0023] Thus, it is 50-8000, as for the viscosity average polymerization degree (henceforth polymerization degree) of obtained PVA-SH, 100-6000 are desirable, and 100-5000 are more desirable. The polymerization degree of PVA-SH is expressed with underwater and the viscosity polymerization degree (P) searched for by the degree type from the limiting viscosity  $[\eta]$  measured at 30 degrees C about this polymer refined after re-saponification according to JIS-K6726. When  $P = ([\eta] \times 103/8.29) (1/0.62)$  degree of polymerization is less than 50, the block copolymer which the reinforcement of a photoresist runs short, the sulfhydryl group installation effectiveness to an end will fall if a degree of polymerization exceeds 8000 on the other hand, and is made into the purpose of this invention is not obtained. Although the saponification degree of PVA-SH used in this invention changes also with classes of denaturation radical and cannot generally be said, from the reinforcement of water solubility and a photoresist, and the point [ substrate ] of an adhesion manifestation, it is desirable that it is [ 50-99.99 mol ] %, it is more desirable, and is still more desirable. [ 70-99.5 mol% of ] [ 60-99.7 mol% of ]

[0024] (Process of a block copolymer) In order to manufacture the block copolymer used for this invention constituent, the radical polymerization of at least one sort of vinyl system carboxylic acids, such as an acrylic acid, a methacrylic acid, a crotonic acid, a maleic acid, an itaconic acid, and a maleic anhydride, these salts, and ester is carried out to the bottom of existence of PVA system polymers, such as said PVA-SH. An acrylic acid and a methacrylic acid are [ especially among these ] desirable. the amount of these vinyl system carboxylic acids used -- the PVA system polymer 100 weight section -- receiving -- the 10 - 100 weight section -- it is 30 - 70 weight section preferably. (Meta) If there is less



amount of the acrylic acid used than this, there will be few amounts of addition of glycidyl (meta) acrylate, and image formation will be impossible. It generates [ if / than this / more / the tuck by the reactant of glycidyl (meta) acrylate ] on the other hand, and is not desirable.

[0025] Although a polymerization can be conventionally performed from those, such as a well-known approach, for example, a bulk polymerization, solution polymerization, a suspension polymerization, and an emulsion polymerization, it is desirable to carry out a polymerization in the solvent which may dissolve a PVA system polymer, for example, the solvent which makes water and dimethyl sulfoxide a subject. Moreover, as a polymerization process, each well-known approach, such as a batch type, half-continuous system, and continuous system, is employable.

[0026] A radical polymerization reaction may use what was suitable for each polymerization system out of well-known radical polymerization initiators, such as - azobisisobutyronitril, and usual radical polymerization initiator, 2 [ for example, ], and 2 '2, 2'-azobis (4-methoxy-2,4-dimethylvaleronitrile), a benzoyl peroxide, diisopropyl peroxy carbonate, potassium persulfate, and ammonium persulfate. For example, in the case of the polymerization in a drainage system, the redox initiation by oxidizers, such as the sulfhydryl group of a PVA end, a potassium bromate, potassium persulfate, ammonium persulfate, a hydrogen peroxide, and a cumene hydroperoxide, is also possible. Also in these initiators, if a potassium bromate and a cumene hydroperoxide are independent, since a radical is not generated, but only redox reaction with the sulfhydryl group of a PVA end decomposes and they generate a radical under the usual polymerization condition, they generate a block copolymer with a PVA system polymer effectively, and, as a result, its water solubility of a photoresist especially improves greatly, and they are desirable. moreover, other polymerization initiators after using a potassium bromate or a cumene hydroperoxide at the time of polymerization initiation or an oxidizer -- additional addition of the hydrogen peroxide may be carried out preferably.

[0027] the amount of these polymerization initiators used -- the PVA system polymer 100 weight section -- receiving -- 0.5 - 5 weight section -- it is 1 - 3 weight section preferably. If there is less amount of the initiator used than this, a polymerization will not advance smoothly, and it is ineffective even if [ than this ] more.

[0028] It faces performing a radical polymerization to the bottom of existence of a PVA system polymer, and it is desirable that a polymerization system is acidity. This is for the rate at which it sets under basicity, and a sulfhydryl group adds and disappears in ion to the double bond of a monomer to become large, and for polymerization effectiveness to fall remarkably, and if it is the polymerization of a drainage system, it is desirable to carry out all actuation by five or less pH preferably six or less pH.

[0029] the range which does not spoil the effectiveness of this invention in carrying out the polymerization of the vinyl system carboxylic acids, such as an acrylic acid and a methacrylic acid, to the bottom of existence of said PVA system polymer -- it is -- an acrylic acid, a methacrylic acid, etc. and a copolymerizable monomer -- coexistence or adding after mixing -- carrying out -- copolymerization -- or block polymerization may be carried out. As such a monomer, for example Olefin acids, such as ethylene, a propylene, and isobutene, Halogenation olefins, such as vinyl chloride, vinylidene-chloride, and vinyl fluoride and vinylidene fluoride Formic-acid vinyl, vinyl acetate, propionic-acid vinyl, BASA tic acid vinyl, Vinyl ester, such as vinyl pivalate, a methyl acrylate, an ethyl acrylate, Acrylic-acid n-propyl, acrylic-acid isopropyl, acrylic-acid n-butyl, Acrylic-acid i-butyl, acrylic-acid t-butyl, 2-ethylhexyl acrylate, Acrylic ester, such as acrylic-acid dodecyl and acrylic-acid octadecyl A methyl methacrylate, ethyl methacrylate, methacrylic-acid n-propyl, Methacrylic-acid isopropyl, n-butyl methacrylate, methacrylic-acid i-butyl, T-butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic-acid dodecyl, Methacrylic ester, such as methacrylic-acid octadecyl, acrylamide, Methacrylamide, diacetone acrylamide, N-methylol acrylamide, A N,N-dimethylacrylamide and acrylamide-isobutane sulfonic acid and the acrylamide system monomers of the sodium salt Nitril, such as acrylonitrile and a methacrylonitrile, an acetic-acid allyl compound, Allyl compounds, such as an allyl chloride, boletic acid, a maleic acid, an itaconic acid, A carboxyl group content compound and its ester, such as a maleic anhydride, phthalic anhydride, trimellitic anhydride, or itaconic acid anhydride, Sulfonic group content compounds, such as an ethylene sulfonic acid, an allyl compound sulfonic acid, a

meta-allyl compound sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, Vinylsilyl compounds, such as vinyltrimetoxysilane, isopropenyl acetate, TORIMECHIRU -(3-acrylamide-3-dimethyl propyl)- Ammoniumchloride, 3-acrylamidepropyl trimethylammoniumchloride, 3-methacrylamide propyl trimethylammonium chloride, The quarternary ammonium salt of N-(3-allyloxy-2-hydroxypropyl) dimethylamine, To the quarternary-ammonium-salt pan of N-(4-allyloxy-3-hydroxy butyl) diethylamine, acrylamide, N-methylacrylamide, N-ethyl acrylamide, N,N-dimethylacrylamide, Diacetone acrylamide, N-methylol acrylamide, methacrylamide, Quarternary ammonium salt, such as N-methyl methacrylamide, N-ethyl methacrylamide, and N-methylolmethacrylamide, Styrene monomer and other N-vinyl pyrrolidone, such as styrene, alpha methyl styrene, P-methyl styrene sulfonic acid and its sodium, and potassium salt, etc. is mentioned. Below the 100 weight sections of the amount of these copolymerizable monomers are desirable to the vinyl system KARUPON acid 100 weight section, and below its 80 weight sections are more desirable.

[0030] (Addition of glycidyl (meta) acrylate) The block copolymer used in this invention adds glycidyl ester, such as glycidyl methacrylate and glycidyl acrylate, to this under existence of a catalyst, after obtaining the PVA system block copolymer which does in this way and contains an acrylic acid, a methacrylic acid, etc. The 0.6-1.5 mols of the amount of the glycidyl ester used in this reaction are 0.8-1.2 mols preferably to one mol of the aforementioned acrylic acid by which addition polymerization was carried out, and a methacrylic acid. The optical bridge formation engine performance of the resist film which will be obtained if there is less amount of the glycidyl ester used than this is low, and sensibility is bad.

[0031] As a catalyst used for the addition reaction of glycidyl ester, well-known catalysts, such as triethyl benzylammonium chloride, triphenyl benzoNIUMU chloride, tetrabutyl ammoniumchloride, triethylamine, and triethylenediamine, are mentioned. Although the conditions of an addition reaction change with classes, such as a compound used for a reaction, and a catalyst, 0.1 - 24 hours of reaction temperature are [ 50-100 degrees C and reaction time ] desirable. the amount of the catalyst used -- the PVA system block-copolymer 100 weight section -- receiving -- 0.01 - 1 weight section -- it is the 0.1 - 0.5 weight section preferably.

[0032] Therefore, the weight ratio with the polymer component (B) containing the metaglycidyl acrylate addition product structure unit expressed with the PVA system polymer component in the aforementioned block copolymer (A), and the above-mentioned formula (I) (meta) It is the  $0.3 \leq \frac{\text{component A}}{\text{Component B}} \leq 1$  that it is the  $0.2 \leq \frac{\text{component A}}{\text{Component B}} \leq 2$  desirable still more preferably, and it is the  $0.5 \leq \frac{\text{component A}}{\text{Component B}} \leq 0.9$  most preferably. If the aforementioned ratio is smaller than 0.2, tuck nature will become large at the resist film obtained from now on. On the other hand, desired photosensitivity will not be acquired if larger than the above-mentioned range.

[0033] In addition to the block copolymer which said glycidyl ester added, in the photosensitive constituent of this invention, further usual polyvinyl alcohol, a polyvinyl pyrrolidone, gelatin, fish GURYU, etc. may be used together.

[0034] (Sensitization agent) As a sensitization agent which is the 2nd indispensable component of this invention constituent, when it is used with said PVA system block copolymer, the compound which can insolubilize a photosensitive constituent to water by optical exposure can be used.

[0035] As such a sensitization agent, the alkyl ether of a benzoin, for example, a benzoin, Benzoin methyl ether, benzoin ethyl ether, benzoin iso-propyl ether, alpha-methyl benzoin, a benzophenone, benzophenone methyl ether, 2 and 2-dimethoxy-2-phenylbenzo phenon, anthraquinone, 1-clo RUANTORAKIN, 2-methyl ANTORAKIN, 2-ethyl anthraquinone, Photopolymerization initiators, such as omega-bromine acetophenone, 2, 4-dimethyl thioxan ton, diethylthio xanthone, p-tert-BUCHIRUTORI chloroacetophenone, alpha-bromine iso butyrophenone, and 1,4-naphthoquinone, are mentioned. The loadings in the photosensitive constituent of this photopolymerization initiator are 0.05 - 2 % of the weight preferably 0.01 to 5% of the weight among total solids. A content is lacking in a photoresist in it being less than 0.01 % of the weight among total solids, on the other hand, if 5 % of the weight is exceeded, at the time of coating, a deposit of a crystal will be seen and a water-soluble desired

photosensitivity constituent will not be obtained.

[0036] (Other monomers) The following monomer which is further photopolymerized under existence of a photopolymerization initiator in addition to the aforementioned block copolymer may be added to the constituent of this invention. The ester of the acrylic acid of the low-grade alkanol which has 1-2 or more hydroxyl groups as such a monomer, or a methacrylic acid, Or the ester of the acrylic acid of a polyethylene glycol with which one side was etherified or esterified, or a methacrylic acid, Or the derivative of the acrylamide or methacrylamide which has at least one free water acid radical in intramolecular, and has the double bond which can be photopolymerized, For example, ethylene glycol (meta) acrylate, ethylene glycol di(metha)acrylate, Triethylene glycol (meta) acrylate, Pori ethylene glycol di(metha)acrylate, Hexandiol (meta) acrylate, neopentyl glycol di(metha)acrylate, Tori propyleneglycol di(meth) acrylate, TORIMECHI roll pro pantry (meta) acrylate, Pen TAERISURITORUTORI (meta) acrylate, beta-oxy-propyl (meta) acrylate, N-beta-oxy-ethyl (meta) acrylamide, N-oxymethyl (meta) acrylamide, N, and N'- bis(beta-oxy-ethyl) (meta) acrylamide, N-alpha, and alpha'-dimethyl-beta-oxy-ethyl (meta) acrylamide etc. is mentioned.

[0037] Moreover, a well-known photopolymerization nature monomer, for example, acrylamide, methacrylamide, meta xylene screw acrylamide, para xylene screw acrylamide, m-phenyl screw acrylamide, ethylenediamine screw acrylamide, hexamethylenediamine screw acrylamide, etc. may permute said a part of monomer with this field conventionally within limits which do not spoil the effectiveness of this invention.

[0038] the loadings of such a monomer -- the block-copolymer 100 weight section -- receiving -- 0.01 - 50 weight section -- it is 0.05 - 30 weight section preferably.

[0039] (Additive) In the photosensitive constituent of this invention, additives, such as a coloring agent which does not bar photopolymerization of the polymerization inhibitor which does not bar photopolymerization of hydroquinone, its derivative, etc., a dispersant, a plasticizer, a defoaming agent, a color, a pigment, etc., can be suitably used together if needed. Moreover, a well-known thermal polymerization inhibitor or a well-known storage stabilizer may be contained in order to raise storage stability.

[0040] (Preparation of a photosensitive constituent) The photosensitive constituent of this invention can be prepared by mixing the aforementioned component. Although it is desirable that it is a water solution as a gestalt of a constituent, you may prepare to the mixed solution of alcohols, such as ethyl alcohol and polyhydric alcohol, and water.

[0041] Using well-known approaches, such as spin coating, DIP coating, roll coating, and bar coating, on various substrates, such as an iron alloy, a copper alloy, and a glass plate, it applies and dries and such a photosensitive constituent forms a sensitization layer. Moreover, it is good also as the so-called dry film resist by applying to front faces, such as plastic film, and drying.

[0042] (Exposure-development) In order to perform image formation using the photopolymer constituent of this invention, after performing the optical exposure of a xenon lamp, an extra-high pressure mercury lamp, a halogen lamp, etc. and performing photopolymerization through a photo mask on the formed sensitization layer, negatives are developed using water and an image is obtained. Thus, \*\*\*\* processing of the obtained resist film is carried out at a hardening solution, and it considers as the hardened material which was further stiffened by postbake and was excellent in endurance after rinsing.

[0043]

[Example] This invention is explained still more concretely based on an example below. In addition, below, unless it refuses, the "weight section" and "% of the weight" are meant especially the "section" and "%", respectively.

[0044] [Example 1]

(Preparation of a PVA system block copolymer) The PVA(M-polymer Kuraray Make: polymerization-degree 510 and saponification degree % of 98.2 mols, and  $[HS] = 1.02 \times 10^{-4}$  eq/g)100 section and the distilled water 900 section which have a sulfhydryl group at the end were taught to the 2l. glass container equipped with a reflux condenser, a dropping funnel, a thermometer, nitrogen entrainment opening, and an agitator. After carrying out the boiling dissolution, introducing nitrogen from nitrogen

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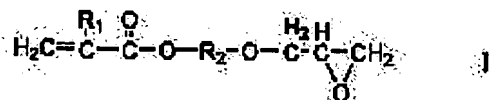
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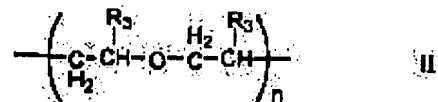
## (54) RESIN COMPOSITION AND ITS HARDENED MATERIAL

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a resin composition being capable of development by use of alkali aqueous solution, having heat resistance and resistance against solvent, and suitable for a permanent resist by making a carboxyl group in a polymer containing at least one carboxyl group contain a compound and a diluent to which a specified compound is added.



**SOLUTION:** A carboxyl group in a polymer containing at least one carboxyl group contains a compound or a diluent to which a compound represented by a formula I is added. Acryl resin is favorably used as the polymer. In the formula I, R1 is hydrogen atom or methyl group, R2 is alkylene, cyclohexane-1, 4-dimethylene or binding chain represented by a formula II, having 2-4 carbon atoms, R3 is hydrogen atom, methyl or ethyl group and (n) is a number of 1-5. It is desirably that the compound represented by the formula I is 4-glycidyletherbutylacrylate.



## LEGAL STATUS

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which may have had the adhesive sensitive plate at the time of a dura mater developed. Visual observation of whether the resist film exfoliates from a substrate top was carried out, and the adhesive property was evaluated.

[0056] O; -- good and \*\*; -- a part -- exfoliation Dura mater processing was performed on condition that the x; exfoliation resolution aforementioned "adhesive property at time of dura mater" evaluation.

Subsequently, it dried by rinsing the processed resist image. The microscope image (2000 times) of the image was copied on the monitor using the IMEDEJIIalpha-II mold (product made from \*\*\*\* Electronic industry), and line breadth was measured. Resolution is so high that the acquired value is small.

[0057] Postbake (for 90 degrees C and 5 minutes) was performed after the same dura mater processing as the corrosion-resistant above of a resist, and the test coupon (42 alloy test coupon: iron nickel alloy) in which the resist carried out full hardening was obtained. The etching machine only for 48Be(s)' ferric chloride liquid performed 50 degrees C and etching for 6 minutes for this, and the sensitization liquid properties of a resist, such as corrosion resistance, were investigated.

[0058] O; -- good and \*\*; -- a part -- defect The corrosion resistance test of the resist which used the metal of stainless steel 304 and copper alloys MF202 (product made from the Mitsubishi \*\*\*\*) and KLF125 (Kobe Steel, Ltd. make) for poor x; pan was also the same result.

[0059] As aforementioned, the water-soluble photosensitivity constituent of this invention has the high adhesion to an alloy, a glass substrate, etc., and the sensitization resist which development is possible, is excellent in photosensitivity, and shows good image formation nature using water is offered. The degree of maximal solution image of a photosensitive resist was what is 4micro and can be satisfied.

[0060]

[Effect of the Invention] Its adhesion to an alloy, a glass base, etc. is high, and since development is possible for the water-soluble photosensitivity constituent of this invention, and it is excellent in photosensitivity, shows good image formation nature and is excellent also in the mechanical strength using water, it is useful also as an ingredient, a protective coat, etc. of the product for which not only a photoresist but detailed structure is needed.

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[Translation done.]